

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 106 496 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the opposition decision:
11.09.1996 Bulletin 1996/37

(51) Int Cl.⁶: **D01F 6/12, C08J 5/18,
B29C 55/30, D02J 1/00**

(45) Mention of the grant of the patent:
06.07.1988 Bulletin 1988/27

(21) Application number: **83305190.7**

(22) Date of filing: **07.09.1983**

(54) **Porous PTFE material**

Poröses Material aus Polytetrafluorethylen
Matériel poreux de polytétrafluoréthylène

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(30) Priority: **10.09.1982 US 416466
10.09.1982 US 416465**

(43) Date of publication of application:
25.04.1984 Bulletin 1984/17

(73) Proprietor: **W.L. GORE & ASSOCIATES, INC.
Newark, Delaware 19714-9206 (US)**

(72) Inventors:

- **Bowman, Jeffery Bruce**
Flagstaff Arizona 86001 (US)
- **Hubis, Daniel Elliott**
Elkton Maryland 21921 (US)
- **Lewis, James David**
Flagstaff Arizona 86001 (US)
- **Newman, Stephen Craig**
Flagstaff Arizona 86001 (US)
- **Staley, Richard Alan**
Flagstaff Arizona 86001 (US)

(74) Representative: **McCallum, William Potter et al**
Cruikshank & Fairweather
19 Royal Exchange Square
Glasgow G1 3AE Scotland (GB)

(56) References cited:

GB-A- 1 505 591	GB-A- 1 590 275
US-A- 3 953 566	US-A- 3 962 153
US-A- 4 049 589	US-A- 4 177 334
US-A- 4 187 390	US-A- 4 250 138

- **Trans. Amer. Soc. Artif. Int. Organs, vol. xx, 1974,
pp. 86-90**
- **Kogyo Zaiyo, Industrial Materials, vol. 25, 1977,
pp. 2, 28-32, with English translation**
- **"Millipore" catalogue, 1975**
- **ASTM D882-79**
- **Laboratory Products Catalogue, Millipore, 1982**

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

EP 0 106 496 B2

Description

This invention relates to porous polytetrafluoroethylene (hereinafter "PTFE") materials having a useful combination of high strength and coarse microstructure, and a method for producing these materials. Articles made from these materials are particularly suitable for use in the medical field.

The products of this invention derived from paste formed products of PTFE. Paste extrusion or paste forming techniques are old in the art and consist of mixing a coagulated dispersion of PTFE resin with a liquid lubricant and forcing the mixture through an extrusion die or otherwise working the lubricated mixture to form a coherent shaped article. The lubricant is then removed, usually by drying, to form a porous, unsintered PTFE article having a density usually within the range of 1.4 to 1.7 gm/cc. Such densities correspond to porosities of 39% to 26%, respectively. At this stage, the article can be raised above its crystalline melt point of about 345°C to sinter it, coalescing the porous material to form a non-porous sintered article.

Alternatively, the unsintered article can be made porous and stronger by stretching according to techniques taught in U.S. Patent No. 3,953,566. Subsequent to stretching, the stretched article can be held restrained and heat treated above the crystalline melt point. In this instance, the article remains porous and when cooled a strong porous article of PTFE is obtained. In the discussions which follow, the term "sintering" is used interchangeably with the process step of raising the unsintered article above its crystalline melting point. U.S. Patent No. 3,953,566 provides a method of producing all kinds of microporous stretched PTFE, such as films, tubes, rods, and continuous filaments. The articles are covered by U.S. Patent No. 4,187,390. The microstructure of these articles consists of nodes interconnected by fibrils.

The key element of the U.S. Patent No. 3,953,566 process is rapid stretching of PTFE. Rapid stretching allows the unsintered article to be stretched much farther than had previously been possible while at the same time making the PTFE stronger. The rapid stretching also produces a microstructure which is very fine in scale having, for example, a very small effective pore size. U.S. Patent No. 3,962,153 describes very highly stretched products, stretch amounts exceeding 50 times the original length. The products of both the 4,187,390 and 3,962,153 patents have relatively high matrix tensile strengths. (See discussion of "matrix tensile strengths" and relation to article tensile strength and density in U.S. Patent No. 3,953,566 at col. 3, lines 28-43).

To compute the matrix tensile strength of a porous specimen, one divides the maximum force required by to break the sample by the cross-sectional area of the porous sample, and then multiplies this quantity by the ratio of the density of the PTFE polymer component divided by the density of the porous specimen. The density of PTFE which has never been raised above its crystalline melt point is 2.30 gm/cc while the density of PTFE which has been sintered or raised above its crystalline melt point may range from above 2.0 gm/cc to below 2.30 gm/cc. For purposes of calculating matrix tensile strength in examples which follow, we have used a density of the PTFE polymer of 2.20 gm/cc for products which have been raised above the crystalline melt point, and a density of 2.30 gm/cc for those which have not.

When the unsintered articles are stretched at slower rates, either limited stretching occurs because the material breaks, or weak materials are obtained. These weak materials have microstructures that are coarser than articles that are stretched equivalent amounts but at faster rates of stretch. The term, "coarse", is used to indicate that the nodes are larger, the fibrils are longer, and the effective pore size is larger. Such coarse microstructure would have further utility if they were strong instead of weak.

According to the present invention there is provided a porous material consisting essentially of PTFE polymer, which material has a microstructure having nodes interconnected by fibrils characterised in that, as measured along at least one direction, it has an average matrix tensile strength greater than 40,000 psi (276 MPa) and an average node height/width ratio greater than 3, an average fibril length greater than 15 µm, and the material is in filament form.

Preferably the average node height/width ratio is greater than 5. Preferably also the average fibril length is greater than 50 µm.

According to a further aspect of the present invention there is provided a porous material consisting essentially of polytetrafluoroethylene polymer, having nodes interconnected by fibrils characterised in that it has an ethanol bubble point of less than or equal to 4.0 psi (27.6 kPa), said fibrils including first fibrils oriented substantially perpendicular to second fibrils, and the ratio of the matrix tensile strength as measured along the first fibril direction to the matrix tensile strength measured along the second fibril direction is between 0.4 and 2.5 and the matrix tensile strength in the weaker direction is greater than or equal to 3000 psi (20.7 MPa).

According to a still further aspect of the present invention, there is provided a process for producing a porous material of polytetrafluoroethylene polymer, which material is characterised by relatively large nodes interconnected by relatively long fibrils and having relatively high matrix tensile strength, the material having been produced from paste-extruded polytetrafluoroethylene extrudate from which all extrusion-aid lubricant has been removed, characterised in that the process comprises the steps:

- (a) increasing the density of the dry extrudate to at least 2.02 gm/cc at an elevated temperature less than the

crystalline melt temperature of PTFE; and

(b) stretching said densified dry extrudate at an elevated temperature less than the crystalline melt temperature.

5 The invention will now be particularly described by way of example with reference to the accompanying drawings, in which:-

Figure 1 is a schematic representation of the microstructure of PTFE material according to the present invention; Figure 2 is a photomicrograph of the PTFE material;

10 Figure 3 is a diagram which shows a characteristic range of the coarseness index and matrix tensile strength obtained by densifying prior to stretching, and a characteristic range in the prior case of not densifying prior to stretching;

Figure 4 is a photomicrograph of the surface of prior art PTFE material that was stretched in one direction;

15 Figure 5 is a photomicrograph of the surface of PTFE material of the present invention that was stretched in one direction;

Figure 6 is a photomicrograph of the cross-section of prior art PTFE material of Figure 4;

Figure 7 is a photomicrograph of the cross-section of PTFE material of Figure 5;

Figure 8 is a photomicrograph of the surface of prior art PTFE material that was biaxially stretched;

Figure 9 is a photomicrograph of the surface of PTFE material of the present invention that was biaxially stretched;

20 Figure 10 is a schematic cross-section of the type of densification die used in Example 3;

Figures 11A and 11B are light microscopy photographs of histological sections through filaments made in accordance with the recent invention and according to the prior art, respectively, showing collagen ingrowth;

Figures 12A and 12B are photomicrographs of the filaments of Figures 11A and 11B, respectively; and

25 Figures 13A and 13B are photomicrographs of other filaments made in accordance with the present invention and according to the prior art, respectively.

A fully densified unsintered article of PTFE is one in which there is no void space and such an article has a density of 2.30 gm/cc. When stretched under the same conditions, it is found that articles which have been densified to near this limit prior to stretching show dramatically coarser structures than articles which have not been densified. There is an increasing effect with increasing densification. The highest densifications produce the most dramatic effect. In order to achieve the highest densification, it is necessary that the densified article be subjected to compressive forces until all void closure is achieved. At a fixed temperature, increased compressive force accelerates the rate of densification, as would be expected. For a given compressive force, densification will occur faster at higher temperatures in the range of 300° C than it will at lower temperatures. Less force may be required to achieve densification at higher temperatures. Higher temperatures, therefore, may facilitate the densification inasmuch as less time and/or less compressive force may be required. However, for otherwise identical conditions, it appears that equivalent stretched articles are obtained independent of whether densification occurs at low temperatures or at high temperatures as long as equivalent densifications are achieved. It appears that the only significant variable is the actual densification achieved as measured by the density of the densified article prior to stretching.

40 Experiments described herein show that when densification conditions are used that result in sintering the material, the material may not be able to be uniformly stretched. Partial sintering is known to occur below 345°C. The conditions that cause sintering, therefore, establish the upper useful limit for the densification temperature.

Densification can be performed through the use of presses, dies, or calendering machines. The use of a calendering machine to densify the dry PTFE enables the manufacturing of long lengths of film.

45 The preferred conditions for densification in a die appear to involve pulling the material through the die at relatively low rates. The force exerted to pull the material through the die may result in stretching the material that has passed through the die. Lower rates required less force to pull the material through the die which results in less stretching of the material. It appears to be desirable to minimize stretching out of the die. Stretching is better controlled in process steps specifically designed to stretch the material.

50 A number of processing steps can be performed prior to densification such as calendering with the lubricant present and stretching with or without the lubricant present. These steps may increase the strength of the final article, but again, such preferred processes have not been detected. Further, it may be preferred to not fully densify the material prior to stretching. It is believed that the densification can be achieved by applying compressive forces in any or all directions and that stretching can subsequently be performed in any or all directions to yield the benefits of this invention.

55 While the fibril lengths and node dimensions are particularly appropriate characteristics for identifying coarse microstructures, they present some problems in quantification. This arises because there is a distribution of node sizes and a distribution of fibril lengths in any given microstructure. Also, somewhat different microstructures are obtained depending on whether the article has been uniaxially stretched, biaxially stretched, or sequentially stretched first in one

direction followed by stretching in a second direction. An idealized drawing of the node-fibril structure for the case of uniaxial stretch of a film is shown in Figure 1. The actual electron micrograph of 198 magnification for this structure is shown in Figure 2.

Articles of the present invention have larger nodes and longer fibrils than prior art materials of similar matrix tensile strength. The four characteristic dimensions of the microstructure are: node height, node width, node length, and fibril length. See Figure 1 for the definition of these dimensions of nodes 2 and fibrils 1 for uniaxially stretched films. Fibril length 3 and node width 4 are measured in the direction of stretching. Node length 6 is measured in the width direction of the film; that is, orthogonal to the direction of stretching, in the plane of stretching. Node height 5 is measured in the thickness direction of the film; that is, orthogonal to the plane of stretching. The distinction between node width and node length may not be obvious for films stretched in more than one direction, since the fibrils may be oriented in many directions and the nodes may be of the same size in more than one direction. In this case, node width is defined as the node dimension in the same direction as the longest fibrils, in the plane of stretching. Node height is measured in the thickness direction of the film; that is, orthogonal to the plane of stretching. The distinction between node length and node height may not be obvious for articles with a symmetrically shaped cross-section, such as circular rods, filaments, and articles with a square cross-section. In this case, node height and node length are said to be the same dimension termed "node height" and this dimension is measured in the direction orthogonal to stretching.

The combination of measurements of two microstructure dimensions and strength in the strongest direction can be used to distinguish between articles of this invention and prior art articles. The combination of the ratio of average node height to average node width, in addition to the average matrix tensile strength in the strongest direction, is useful for characterizing articles of the present invention.

For materials that have been biaxially stretched, or stretched first in one direction followed by stretching in a second direction, there is some difficulty in precisely quantifying the geometry of the node-fibril structure. Materials that have been stretched in more than one direction have a greater range of distribution of microstructure dimensions. For this reason, coarseness has also been defined in terms of other properties and particularly in terms of the ethanol bubble point (EBP), which is a measure of the maximum pore size in the test specimen (see ASTM F316-80). Specifically, the EBP is the minimum pressure required to force air through an ethanol-saturated article of this invention. Raising the pressure slightly should produce steady streams of bubbles at many sites. Thus, the measurements are not biased by artifacts such as puncture holes in the material. Ethanol bubble point is inversely related to pore size; lower values of EBP indicate larger pores, or in the terminology of this application, coarser structure. It is believed that EBP can be assumed to be independent of the length of the path that the air travels through the article. In other words, it is believed that EBP provides a characterization of pore size that is not unacceptably dependent on the dimensions of the tested article.

In an article which has first fibrils oriented in a first direction substantially perpendicular to second fibrils oriented in a second direction, an EBP less than 20.7 kPa (3.0 p.s.i.) is desirable (for example about 8.3 kPa (1.2 p.s.i.) with a matrix tensile strength ratio, relative to the first and second directions, of between 0.5 and 2.0, preferably between 0.67 and 1.5.

Another indicator of coarse structure is relatively low resistance to the passage of air (Gurley number). Gurley number is defined as the time in seconds for 100 cc of air to flow through one square inch (6.5 sq.cms) of material for a pressure of 1.2 kPa (4.9 inches of water) across the material. See ASTM D-726-58 for a method of measuring the Gurley number.

In order to provide a basis for comparison of coarseness for articles that have been densified to different densities and subsequently stretched, a "coarseness index" is defined here as the density of the stretched porous article divided by the EBP of that article. Density is an indicator of total pore volume. Should two articles be of the same density, the article with the lower EBP is said to be coarser. Should two articles have the same pore size, the article with the higher density is said to be coarser. Thus, the coarseness index is directly proportional to density and inversely proportional to EBP. An increase in coarseness is indicated by an increase in the coarseness index. Introducing the density in combination with EBP provides means of comparing prior art articles with articles of this invention over a wide range of matrix tensile strengths.

Sintering a restrained stretched article does lower the EBP of the article, and usually increases the coarseness index. However, in some cases the coarseness index may not increase due to sintering since the density of the article may be lowered by sintering.

Figure 3 present a graph of the variables, coarseness index and matrix tensile strength. Porous material and articles not heretofore available are produced with the present invention to have a matrix tensile strength greater than or equal to about 3,000 psi (20.7 MPa) and have a corresponding coarseness index greater than or equal to the value on a line connected by the points A,B,C, and D. The coordinates of these points are as follows: Point A [3,000 psi (20.7 MPa), 0.40 (gm/cc)/psi (58gm/cc/MPa)], Point B [12,000 psi (82.2 MPa), 0.40 (gm/cc)/psi (58 gm/cc/MPa)], Point C [16,000 psi (110.4 MPa), 0.20 (gm/cc)/psi (29 gm/cc/MPa)] and Point D [25,000 psi (172.5 MPa), 0.20 (gm/cc)/psi (29 gm/cc/MPa)]. Points C and D could alternatively have coarseness indices of 0.23. Again, points

A,B,C and D could alternatively have coarseness indices of 0.45 (gm/cc)/psi (62.25 gm/cc/MPa). The crushability (as hereinafter defined) of such porous material is less than 10%.

Examples are not given for films processed at stretch ratios exceeding about 4:1 in a direction. Higher stretch ratios generally result in articles with higher matrix tensile strengths, as described in U.S. Patent No. 3,953,566. No evidence exists to suggest that films of the present invention cannot be stretched further to obtain higher strength while still maintaining coarser than prior art films of the same length. It is expected that processing films at higher stretch ratios will certainly yield films of this invention with matrix tensile strengths exceeding 25,000 psi (172.5 MPa).

Points in the region corresponding to the present invention were derived from data presented in the examples that follow. The EPB and matrix tensile strength measurements were performed subsequent to sintering the restrained, stretched articles. The conditions of sintering are described in the examples. The matrix tensile strength value used was the value corresponding to the strongest direction of the material. This representation of coarseness and strength is useful for characterizing materials that are stretched in one or more directions prior to or subsequent to sintering.

The representation of coarseness index and strength in Figure 3 is specific to unfilled porous PTFE articles. Porous PTFE articles may be filled with substances such as asbestos, carbon black, pigments, and mica, as taught by U.S. Patent Nos. 3,953,666 and 4,096,227. Articles of the present invention can be likewise filled. The presence of a filler, however, may affect the measurement of coarseness index since EBP is a function of the surface tension of the porous article and the filler may affect the surface tension of the article.

Articles of the present invention, therefore, can be characterized in several ways. Either coarseness index or the node height to node width ratio, in conjunction with matrix tensile strength in the strongest direction, can be used to describe the same products of the present invention. That is, coarseness index and the node height to node width ratio are not independent parameters; both describe the structure of articles of the present invention. Coarseness index is particularly useful for describing the structure of thin films in which maximum node height is limited by the thickness of the film. The node height to node width ratio is particularly useful for describing the structure of articles too small to enable the measurement of the EBP. In many cases, either of these parameters can be used to describe the structure of the same articles.

Films of this invention that have strength of similar magnitude in orthogonal directions can be distinguished from prior art films by the characterization of matrix tensile strength in orthogonal directions and EBP. This characterization includes sintered films having the ratio of matrix tensile strengths in orthogonal directions within the range of 0.4 to 2.5, where the weaker direction has a matrix tensile strength greater than or equal to about 3000 psi (20.7 MPa). Films of this invention that satisfy these strength requirements have an EBP less than or equal to about 4 psi (27.6 kPa).

Unsintered articles extruded from preferred resins can be stretched farther and more uniformly to achieve stronger stretched products than unsintered articles extruded from non-preferred resins. The preferred resins are highly crystalline (such as Fluon CD123 supplied by ICI-Fluon being a Registered Trade Mark) but other resins can also be used in practicing this invention. (See U.S. Patent Nos. 4,016,345 and 4,159,370).

Processes which might appear to put the unsintered article under a compressive force, but do not achieve densification, can yield results which are not consistent with the teachings of this invention. For example, U.S. Patent No. 4,250,138 teaches a drawing step which might appear to be consistent with the process described in Example 3 herein. Yet the opposite effect is achieved; i.e. finer structures are obtained as indicated by increased EBP. U.S. Patent Nos. 4,248,924 and 4,277,429 teach a method of applying compressive forces to a film which might appear to be consistent with the densification step described herein. Again, the opposite effect is achieved; i.e. the prior art process is practiced to diminish the pore size of one side of a film relative to the other side.

The conditions under which the densified article is stretched greatly affect the microstructure that is obtained. Higher rates of stretching yield progressively finer microstructures, and there is the same qualitative interaction of rate of stretch and temperature during stretching that is described in U.S. Patent No. 3,953,566. Thus, densified unsintered articles can be stretched under conditions that will yield products that are similar to prior art products, such as those taught in U.S. Patent Nos. 4,187,390 and 3,962,153. The process of the present invention can also yield products with characteristics not heretofore available. It is these latter materials which are sought to be uniquely identified by the values of parameters set forth in the claims.

The experiments that comprise the examples that follow demonstrate that for otherwise identical processing conditions, the addition of the densification step produces coarser articles as compared to prior art articles of comparable strength. The coarseness was characterized by permeability, largest pore size, and dimensions of the nodes and fibrils. Materials produced with the densification step were seen to have nodes that extended through the thickness of the article (i.e. in the direction orthogonal to the direction(s) of stretch). This structure in a film or tape may result in higher peel strength, and/or higher tensile strength in the thickness direction, and/or higher compressive strength in the thickness direction.

Biaxially stretched films of the present invention have usefulness as surgical reinforcing membranes. Uniaxially stretched filaments of the present invention have usefulness as sutures and ligatures. These articles are both strong and possess coarse microstructures. Coarse microstructures are desirable in medical applications because they allow

cellular ingrowth and incorporation of body tissue. Films of the present invention can be useful in the manufacture of coaxial cables because they are both crush-resistant and porous. Films of the present invention also can be useful in applications demanding tensile strength in the thickness direction.

The following examples which disclose processes and products according to the present invention are illustrative only and are not intended to limit the scope of the present invention.

Example one

Films that are uniaxially stretched

PTFE resin (Fluon CD123, ICI) was paste-extruded as a film extrudate and calendered. The calendered film was then dried to remove the extrusion aid. The properties of the dry, calendered film were as follows: thickness of about 0.016 inch (0.04 cm), density of about 1.6 gm/cc, matrix tensile strength in the direction of extrusion of 1.6×10^3 psi (11 MPa), and matrix tensile strength in the transverse (width) direction of 0.6×10^3 psi (4.14 MPa). The dry, calendered extrudate was cut into approximately 4.5 inch by 4.5 inch (11.4 cm square) specimens.

Some of the specimens were then densified by compression in a Carver press that could be heated; the remaining specimens were left undensified at the 1.6 gm/cc density level to serve as test controls. Gage blocks were used between the flat compression plates (and alongside the specimens) to control density by allowing densification only to predetermined thicknesses. In some cases, the gage blocks used were thinner than the thickness that was calculated to yield the desired density. These thinner blocks were required because some of the samples would regain some of their thickness after the compressive forces were removed. A range of densities was examined from 1.6 gm/cc ("control"-undensified) to values approaching the maximum achievable density, 2.3 gm/cc. Densifications were carried out at temperatures from ambient (22°C) to slightly above 300°C. The times to reach the desired densification temperature and the times to reach the desired densification at these temperatures were noted. The "control" pieces were subjected to the same temperature and time conditions as were used in densification. For convenience, two film samples were stacked together with a sheet of Kapton (R.T.M.) polyimide film (DuPont) between them so that two 4.5 inch by 4.5 inch (11.4 cm square) samples of film could be simultaneously densified.

The following steps were used to densify the dry PTFE film:

1. Carver press platens heated to specified temperature;
2. Film inserted between two flat steel plates along with Kapton polyimide film to serve as a release agent;
3. Gage blocks placed on perimeter of sheet. (Gage blocks not used for densification to maximum density);
4. Plates, with film between, placed inside press;
5. Platens closed until contact made;
6. Steel plates heated to desired temperature for densification;
7. Pressure applied and both steel plates slowly brought into contact with the thickness gage blocks (or specimen, if gage blocks not used);
8. Pressure held for sufficient time to obtain desired densities;
9. Pressure released;
10. Materials densified at higher than ambient temperatures cooled in water upon removal from the press.

The 4.5 inch by 4.5 inch (11.4 cm square) specimens were weighed prior to the densification step. Thickness measurements were taken at the four corners, at about one inch (2.54 cms) from each edge, and these four readings were averaged. The density was calculated by dividing the weight of the specimen, by the area times the average thickness. This procedure yields a nominal density of the specimen, since the thickness of the specimen varied due to local inconsistencies.

Materials (densified and undensified) were then stretched on a pantograph in the longitudinal direction (i.e., the primary direction of both extrusion and calendering) to accomplish stretching. The pantograph used was capable of stretching 4.5 inch by 4.5 inch (11.4 cms square) samples of film to yield 4 inch by 16 inch (10 cm by 41 cm samples for uniaxial stretching. (An extra 0.25 inch (0.64 cm) length was required on each side of the specimens to accommodate clamping of the material in the machine). The 4.5 inch by 4.5 inch (11.4 cms square) film was gripped on each side by 13 actuated clamps, which could be moved apart uniformly on a scissor mechanism at constant velocity to stretch the film. The film was heated to the desired temperature for stretching, by heater plates directly above and below the 4.5 inch by 4.5 inch (11.4 cms square) samples.

The stretch conditions were:

Temperature: approximately 300°C
Stretch ratio: 4:1 (300% increase in length)

Stretching rate: approximately 400%/sec.

(determined by dividing the percent change in length by the duration of the stretching operation)

The stretched specimens were then restrained from shrinking, by placing them on a pinframe, and immersed in a 370°C salt bath for about 20 seconds, thereby sintering the specimens.

Temperature did not appear to significantly affect the densification process. Therefore, the data reported in Table 1 are averages of the measurements obtained for given densities irrespective of the densification temperature.

All data for matrix tensile strength, fibril length, and node width are reported for measurements made in the direction of stretch (which is also the primary direction of extrusion and calendaring). Break forces were measured using specimens with a 1 inch (2.5 cms) gage length; the tensile tester cross-head speeds were 10 inches (25 cms) per minute. The density prior to stretching is listed as a single number and is the aforementioned nominal value. The actual densities after densification varied due to experimental variability and inevitable small measurement error. Thus, the individual measurements for the 1.63 gm/cc materials ranged from 1.60 to 1.64 gm/cc. The individual measurements for the 1.83 gm/cc materials ranged from 1.75 to 1.85 gm/cc. The individual measurements for the 2.01 gm/cc materials ranged from 1.97 to 2.04 gm/cc. The individual measurements for the 2.27 gm/cc materials ranged from 2.19 to 2.35 gm/cc. Therefore, the nominal range of 2.27 gm/cc includes the maximum obtainable densities.

Figures 4 and 5 present scanning electron micrographs of the surfaces of final specimens (stretched and sintered) that had not been previously densified (nominal density of 1.63 gm/cc), and that had been previously densified to 2.27 gm/cc (nominal) prior to stretching respectively. The magnifications for the left and right sides of these two micrographs (Figure 4 and 5) are about 155 and 1550, respectively. These micrographs readily demonstrate the difference in "coarseness" due to the effect of densification. Figure 6 and 7 present scanning electron micrographs of the cross-section of the same two final specimens that had not been previously densified, and that had been previously densified (2.27 gm/cc), respectively. The magnifications for the left and right sides of the micrograph in Figure 6 are about 152 and 1520, respectively. The magnifications for the left and right sides of the micrograph in Figure 7 are about 147 and 1470, respectively. Again, the difference in coarseness is clear. These micrographs also demonstrate the difference in node height through the cross-section. The material produced by the process of this invention not only has nodes of greater heights compared to the material that had not been densified, but a significant number of the nodes are seen to extend completely through the cross-section, unlike the case of the undensified material. These micrographs are representative of all of the undensified control materials (1.63 gm/cc) and materials that had been densified at the density level, a 2.27 gm/cc, regardless of densification temperature. The difference in coarseness as is apparent in Figure 4 and 5 and Figures 6 and 7 is reflected in the fibril length and node width measurements presented in Table 1. The materials made in accordance with the process of the present invention had longer average fibril lengths and wider average node widths than materials that were not densified prior to stretching, but which had received other identical processing. Equally important, the data in Table 1 show the average matrix tensile strength in the stretch direction for all materials that had been densified prior to stretching to be at least of the same order of magnitude as the undensified, control materials. The combination of long fibril lengths, wide node widths, and high matrix tensile strengths relative to prior PTFE materials available from conventional processes is surprising.

Returning to Table 1, the fibril lengths and widths of the nodes (in the direction of stretching) were measured from scanning electron micrographs of cross-sections of the stretched, sintered materials in order to assess relative coarseness based upon the dimensions of the microstructure. The fibril length and node width measurements utilized scanning electron microscope pictures of about 150X magnification and dual magnification of 10X (about 1500X original), and the following steps:

1. SEM pictures were marked with two lines spaced approximately 24 mm apart, using a plexiglass fixture;
2. The fibril lengths were then determined using dividers to measure the internodal spacing along the outside edge of the line starting at the upper left corner of the picture at the first distinct node spacing. The divider was then placed on a scale that accounted for the magnification factor and the lines were read to the nearest half μm , and values recorded. This procedure was repeated for the next consecutive node spacings along this line and each measurement recorded;
3. The procedure was repeated to measure node widths instead of space between nodes, and the data recorded.

Examination of these data shows that the materials that were densified to a maximum degree, that is, in the 2.27 gm/cc range, (and subsequently stretched and sintered) were significantly coarser than the other materials, as evidenced by the longer fibrils and wider nodes. The Table 1 data are exemplary and show stretched materials that were densified less than 2.27 gm/cc prior to stretching had longer fibril lengths and wider node widths than the control pieces, but that the 2.27 gm/cc range materials had markedly coarser structures with no appreciable loss in matrix tensile strength.

The data pertaining to Gurley number can characterize the coarseness of these materials. Lower values of this

parameter indicate greater permeability of the structures. Permeability and, therefore, Gurley number measurements, are strongly dependent on path length. The use of Gurley number is an appropriate means of comparing the articles described in this example, however, since the materials were processed identically except for the densification step. The data pertaining to ethanol bubble point (EBP) also can characterize the coarseness of materials. Lower values of this parameter indicate greater maximum pore size of the structures. Greater permeability, as well as larger pore size quantify greater coarseness. The data in Table 1 demonstrate the materials densified to about 1.83 and 2.01 gm/cc, upon stretching, exhibit lower values of the respective parameter than the 1.63 gm/cc control materials, and that the 2.27 gm/cc range materials had a markedly higher permeability and larger pore sizes than the 1.63 gm/cc control materials. The final materials that had been densified in the range of 2.27 gm/cc did have markedly lower values for these parameters than those materials that had been densified less.

The crushability test data in Table 1 demonstrate a macroscopic manifestation of the coarse microstructure available through the present invention. In this test, the specimens were placed under a tensile load by applying a 0.5 lb (0.22 kg) force to the material in direction of stretching. A thickness measurement was taken which constituted the original thickness. Next, an 18 oz (0.5 kg) weight of .012 square inch (.077 sq cm) area was applied to the specimen for 0.5 minutes and the resulting thickness recorded with the weight still applied. Percent crush, or crushability, is defined as $(t-c)/t$ (100%), in which "t" is the original thickness, and "C" is the thickness under load. Lower values of crushability, therefore, indicate a higher resistance to being crushed (i.e., a higher crush-resistance). A crushability of less than 10% is desirable; preferably less than 8% and more preferably less than 5%.

Again the most remarkable feature of these data is the difference in crushability between the materials densified to about 2.27 gm/cc, although the materials densified to lower densities did show improved resistance to crushing over the undensified materials. The materials densified to about 2.27 gm/cc exhibited significantly greater resistance to being crushed as evidenced by lower crushability.

The testing data indicate that densifying the dry, calendered extrudate to about 2.27 gm/cc or greater (i.e., the range of highest densities) prior to stretching had an especially pronounced effect on the "coarseness" of the stretched, heat treated PTFE materials without detracting from the matrix tensile strength.

Other samples were subsequently processed in essentially the same manner in order to examine the utility of higher densification temperatures. The same ranges of density prior to stretching as used in the above-mentioned experiments were examined for higher ranges of densification temperature. Consistent results were not obtained with materials subjected to elevated densification temperatures. Many of the final specimens were grossly non-uniform in appearance, unlike any of the final specimens that had not been subjected to these elevated temperatures prior to stretching. Some of the retained samples that had been densified under identical conditions, but not stretched, were subjected to differential scanning calorimetry analysis. The identification of reduced heats of fusion for these materials compared to unprocessed resin indicated that the samples had been sintered to some extent. The unintentional sintering was attributed, in part, to non-uniformity of temperature across the plate. The important finding, however, is that partially or completely sintered materials, whether densified or not, cannot be stretched to yield uniform final materials for the above-mentioned stretch conditions.

The following conclusions can be reached from these tests:

1. The densification-stretching process yields high strength, coarse microstructure materials when extrudate is densified to 2.27 gm/cc. The 2.27 gm/cc density actually refers to a range of densities obtained. The maximum achievable density is included in this range.
2. The inclusion of a "dry" densification step (that is, with lubricant removed from the extrudate) of any degree of densification prior to stretching does not compromise the matrix tensile strength of the stretched material.
3. Densifying dry extrudate to a density of 2.27 gm/cc prior to stretching results in a stretched material with a coarse structure, quantified by EBP, Gurley number, node width and fibril length measurement. By comparison, densifying to lower densities, or not at all, prior to stretching results in a stretched material with a finer structure.
4. Densifying dry extrudate to a density of 2.27 gm/cc prior to stretching results in a more crush-resistant stretched material than if the dry extrudate is densified less, or not at all.
5. The degree of densification (as quantified by density measurements) has a very pronounced effect on the properties of the stretched material. The degree of densification essentially describes the salient feature of the densification process provided that the material has not been sintered.
6. The influence of temperature is to serve as a process catalyst. Less time is required to reach the desired density in the densification step for higher densification temperatures. Increased temperature of densification may allow the use of lower compressive forces in order to achieve densification.
7. The preferred densification conditions are those that do not result in any sintering of the dry extrudate.

EP 0 106 496 B2

TABLE 1

Properties of the final specimens**				
Density prior to stretching				
	1.63±.01 gm/cc* (Control)	1.83±.02 gm/cc (Comparison)	2.01±.02 gm/cc (Comparison)	2.27±.05 gm/cc
Thickness (inch)	.0119±.0002	.0118±.0002	.0114±.0002	.0112±.0005
(cm.)	.0302±.0005	.03±.0005	.029±.0005	.0284±.0013
Density (gm/cc)	56±.02	.57±.02	.59±.02	.58±.04
Matrix tensile strength (psi)	15,600±700	15,700±900	15,900±600	16,500±100
(MPa)	107.6±4.8	108.3±6.3	109.7±4.1	113.9±6.9
Fibril length (µm)	4±1.	5±1.	5±1.	23±4.
Node width (µm)	3±1.	3±1.	4±1.	15±3.
EBP (psi)	7.8±.5	6.9±.4	6.4±.6	2.5±1.0
(kPa)	54±3.4	47.6±2.8	44.2±4.1	17.3±6.9
Gurley number (seconds)	27.5±3.8	23.8±3.5	19.4±3.5	6.5±2.4
Crushability (%)	15±1.	14±2.	14±2.	9±2.
Coarseness index [(gm/cc)/psi]	.07	.08	.09	.23
(gm/cc/MPa)	10.1	11.6	13	33.3

**All values are rounded. The values presented are the means ± one standard deviation calculated from the mean values for each specimen produced at each density level prior to stretching.

*Control with no densification step.

Example two

Films that are biaxially stretched

Four other 4.5 inch by 4.5 inch (11.4 cm.sq.) samples of film of the type described in the first paragraph of Example One above were stretched in the pantograph machine. In this case, three samples were densified in the Carver press at temperatures of about 300°C and a fourth sample was subjected to the same thermal conditions, but not densified. The undensified material served as a test control. The materials were densified in essentially the same manner as described in the third paragraph of Example One.

All four samples were stretched simultaneously in two directions at right angles to each other in the pantograph machine (described in Example One), 100% in each direction. Thus, the surface area of the stretched film was four times greater than the surface area of the original film. The film temperature was about 300°C at the start of the

stretching operation. Stretching rates of about 130% per second in each direction were used. Stretching rate was determined by dividing the percent change in length by the duration of the stretching operation. (The clamps of the pantograph moved apart at constant velocity). The stretched specimens were then restrained from shrinking by placing them on a pinframe, removed from the pantograph machine clamps, and immersed in a 370°C salt bath for about 20 seconds, thereby sintering the specimens at least in part. The specimens were then cooled in water to yield the final specimens.

The data in Table 2 show the effects of this invention. Figures 8 and 9 present scanning electron micrographs of the surfaces of the control material (1.61 gm/cc) and the material that had been densified to 2.25 gm/cc, respectively. The magnifications for the left and right sides of these micrographs in Figures 8 and 9 are about 150 and 1500, respectively. The relative coarseness of the material that had been densified to 2.25 gm/cc is readily apparent. These figures demonstrate the structural differences due to the invention that result in the difference in ethanol bubble points as indicated in Table 2. The micrograph in Figure 9 is representative of the structure that resulted due to the inclusion of the densification step. The final material is not completely uniform, however, and some regions are not seen to be as coarse with regard to the dimensions of the microstructure as other regions of the same material. This non-uniformity is attributed to local inconsistencies during the densification.

The data in Table 2 show that the material that was densified the most prior to stretching was far more crush-resistant than the materials that were densified less or not at all. Four additional samples were produced from the same raw materials using the same processes in order to further examine the benefits of the present invention with respect to crush-resistance. The same range of densities prior to stretching was examined. These samples, unlike those whose data appear in Table 2, were not sintered subsequent to stretching. The data for these materials that were not sintered appear in Table 3. The crushability for the stretched materials with pre-stretching densities of 1.63, 1.89, 2.06, and 2.29 gm/cc were 30.1, 19.7, 10.2, and 3.6%, respectively, showing that those materials that were densified the most produced the most crush-resistant final products. Comparing the data for the sintered and unsintered materials that were not densified indicates that sintering serves to decrease crushability for undensified materials (from 30.1% to 14.6%, in this case). The material that was densified the most but not sintered was still far more crush-resistant (a crushability of 3.6%) than the undensified material that was sintered (which had a crushability of 14.6%).

Break forces were measured using specimens with a 1 inch (2.54 cms) gage length; the tensile tester cross-head speed was 10 inches (25.4 cms) per minute. The longitudinal direction is the primary direction of extrusion and calendaring. The transverse direction is orthogonal to the longitudinal direction, in the plane of stretch.

TABLE 2

Properties of the final specimens**				
Density prior to stretching				
	1.61 gm/cc* (Control)	1.83 gm/cc (Comparison)	2.02 gm/cc	2.25 gm/cc
Thickness				
(inch)	.0111	.0109	.0105	.0122
(cm)	.0282	.0277	.0267	.0310
Density				
(gm/cc)	.57	.54	.65	.54
Ethanol bubble point				
(psi)	9.8	7.0	3.6	1.2
(kPa)	67.6	48.3	24.8	8.28
Longitudinal matrix tensile strength				
(psi)	10,100	8,300	7,000	6,500
(MPa)	69.7	57.3	48.3	44.9
Transverse matrix tensile strength				

**All values are rounded

*Control with no densification step.

EP 0 106 496 B2

TABLE 2 (continued)

Properties of the final specimens**				
Density prior to stretching				
	1.61 gm/cc* (Control)	1.83 gm/cc (Comparison)	2.02 gm/cc	2.25 gm/cc
(psi)	10,200	11,200	8,600	6,400
(MPa)	70.4	77.3	59.4	44.2
Coarsness index				
[(gm/cc)psi]	.06	.08	.18	.45
(gm/cc/MPa)	8.7	11.6	26.1	65.2
Crushability				
(%)	14.6	17.0	16.6	4.2

**All values are rounded

*Control with no densification step.

TABLE 3

Properties of the final specimens that were not sintered after stretching**				
Density prior to stretching				
	1.63 gm/cc* (Control)	1.89 gm/cc (Comparison)	2.06 gm/cc (Comparison)	2.29 gm/cc
Thickness				
(inch)	.0146	.0130	.0120	.0116
(cm.)	.0371	.0330	.0305	.0295
Density				
(gm/cc)	.58	.63	.61	.72
Ethanol bubble point				
(psi)	14.2	8.1	4.8	3.1
(kPa)	98.0	55.9	33.1	21.4
Longitudinal matrix tensile strength				
(psi)	4,400	4,300	4,800	3,800
(MPa)	30.4	29.7	33.1	26.2
Transverse matrix tensile strength				
(psi)	2,400	2,200	2,800	2,400
(MPa)	16.6	15.2	19.3	16.6
Coarsness index				
[(gm/cc)psi]	.04	.08	.13	.23
(gm/cc/MPa)	5.8	11.6	18.8	33.3
Crushability				
(%)	30.1	19.7	10.2	3.6

**All values are rounded

*Control with no densification step.

Example 3

Filaments that are uniaxially stretched

5 Part A

Part A illustrates the effect a densification die can have on the microstructure of a uniaxially stretched filament. The processing of the two finished filaments described herein was adjusted to yield materials with equivalent diameters, densities, and matrix tensile strengths.

10 PTFE dispersion powder ("Fluon CD-123" resin produced by ICI America) was blended with 130 cc of "Isopar M" odorless solvent (produced by Exxon Corporation) per pound of PTFE, compressed into a pellet, and extruded into a 0.106 inch (0.27 cm) diameter filament in a ram extruder having a 95:1 reduction ratio in cross-sectional area from the pellet to the extruded filament. (Isopar is a trade mark)

15 The Isopar M was evaporated from a sample of the extruded filament. The density of this sample was about 1.49 gm/cc, and its matrix tensile strength was about 900 pounds per square inch (6.2 MPa).

The extruded filament still containing Isopar M was immersed in a container of Isopar M at 60°C, and stretched nine-fold (800%) between capstans with an output velocity of about 86.4 ft/min (26.3 m/min). These capstans had a diameter of about 2.8 inches (7.1 cms) and a center-to-center distance of about 4.5 inches (11.4 cms). The diameter of the filament was reduced from about 0.106 inch (0.269 cm) to about 0.039 inch (.099 cm) by this stretching. The 20 Isopar M was removed from this stretched material. The density of the stretched filament was about 1.3 gm/cc, and the matrix tensile strength was about 5,400 pounds per square inch (37.3 MPa).

The stretched filament, from which the Isopar M had been removed, was then pulled through a circular densification die heated to 300°C. The output velocity of the material exiting the die was about 7.2 ft/minute (2.2 m/min). The opening in the die tapered at a 10° included angle from about .050 inch diameter (.013 cm) to .030 inch (.076 cm) diameter, 25 and was then constant for a land length of about .030 inches (.076 cm).

The die diameter of .030 inches (.076 cm) was chosen on the basis of two assumptions:

1. It was desirable to densify the stretched filament to approximately 2.2 gm/cc.
2. There would be no weight/meter change of the stretched rod as it underwent densification. Using these assumptions, die diameter was calculated to represent the reduction in cross-sectional area necessary to increase the 30 density of the stretched rod to about 2.2 gm/cc. In the specific case of the A-16 filament, that calculation was worked as follows:-

$$\begin{aligned}
 D_2 &= \left(D_1^2 \times \frac{\rho_1}{\rho_2} \right)^{1/2} \\
 &= \left(.039^2 \times \frac{1.3}{2.2} \right)^{1/2} \\
 &= 0.030 \text{ inches (.076 cm)}
 \end{aligned}$$

40

D_1 = initial diameter of stretched rod in inches

D_2 = die diameter in inches

ρ_1 = initial density of stretched rod in gm/cc

ρ_2 = nominal value of void-free PTFE as 2.2 gm/cc

45

Removing a piece of filament from the die, by halting the densification process and pulling the material back through the entrance of the die, showed that when the stretched filament was pulled through the densification die it developed a translucent segment characteristic of PTFE having a density of about 2.2 gm/cc. This segment corresponded to the .030 inch (.076 cm) land length section in the die immediately following the 10° included angle transition (see Figure 10).

50 As the material exited the die, however, it once again developed a white appearance characteristic of PTFE having a density less than about 2.2 gm/cc. This is because the force necessary to pull the stretched filament through the die is sufficient to cause some stretching of the material after it leaves the die. This was confirmed by measuring the weight/meter of the material pre- and post-die. A decrease in weight/meter was noted in the material post-die, indicating stretching took place. Subsequent experimental work demonstrates that die diameters both greater and smaller than .030 inches (.076 cm) can also effect the desired change in microstructure. The important consideration in choosing a die diameter is that it changes the cross-sectional area of the stretched rod so as to achieve a material density in the die greater than or equal to about 2.0 gm/cc. There is an increasing effect on structure with increasing densification.

55

The stretched filament, which had been pulled through the die, was then heated in a 300°C oven and further

stretched seven-fold (600%), from an initial length of about 7.2 inches (18.3 cms), in a batch manner with a constant velocity of about 37 ft/min (11.3 m/min).

Finally, the filament was restrained from shrinking and heated in a 367°C oven for 30 seconds.

As described in Table 4, the filament (A-16) from the final heat treatment had a density of about 0.4 gm/cc, a diameter of about 0.022 inch (0.56 cm), and a matrix tensile strength of about 49,000 pounds per square inch (338 MPa). The structure was comprised of nodes of apparently solid PTFE interconnected by fibrils. The average fibril length was about 120 μ m, the average node width about 17 μ m (measured in the direction of stretch), and the average node height about 102 μ m (measured orthogonal to the direction of stretch). The filament underwent a total stretch ratio of 79:1 from the extrudate stage. This was calculated by dividing the dried filament extrudate weight/meter by the finished filament weight/meter.

One end of a length of the A-16 filament was heated, densified and then swaged onto a standard 0.022 inch (0.056 cm) diameter surgical needle, making a prototype suture with matching needle and thread diameters. This needle/thread combination is not currently available in the marketplace and has the potential advantage of reducing suture line bleeding in vascular anastomoses. This material was sewn into the tissue of a guinea pig and harvested after 30 days. Fibroblast cells had penetrated into the structure of the suture, and substantial collagen was formed throughout the inner structure of the suture (see Figure 11A). Also, the suture became well embedded in the tissue. These attributes, combined with the material's strength and ease of handling, should make it useful as a suture.

Another material (3-1-3) was manufactured using a process similar to that described above with the major exception that the stretched filament was not pulled through a densification die. Minor processing changes were necessary to achieve this equivalence. Specifically, the extruded filament had a diameter of about .090" (.229 cm), a matrix tensile strength of about 1200 psi (8.3 MPa) and it underwent a total stretch of 52:1 through the process. Table 4 demonstrates that this material has a diameter, matrix tensile strength, and density nearly identical to that of the material which had been pulled through the die.

When implanted in guinea pigs this material (3-1-3) permitted only minimal collagen penetration (see Figure 11B).

As illustrated by the pictures in Figures 12A and 12B and information in Table 4, these materials have vastly different microstructures. The A-16 material had much longer fibril lengths, and nodes where its height/width (H/W) ratio was substantially greater than in the undensified (3-1-3) material.

For materials with matrix tensile strengths greater than about 15,000 psi (103.5 MPa) this node relationship of H/W is unique. Previously, only those materials with matrix tensile strengths less than about 15,000 psi (103.5 MPa) had a node H/W ratio greater than or equal to 3. Conversely, when prior art matrix tensile strengths get above about 15,000 psi (103.5 MPa), the node H/W ratio drops below about 3. The only materials with matrix tensile strengths greater than or equal to about 15,000 psi (103.5 MPa) having a node H/W ratio greater than or equal to about 3 are those materials which undergo a densification step prior to stretching, where the densification increases the specific gravity of the material to greater than or equal to about 2.0 g/cc. It appears from this example, that densification prior to final stretching may yield filaments having longer fibril lengths than would be achieved with similar amounts of stretch in a process not including a densification step.

Part B

The following example further illustrates the effect of the densification die on microstructure. No attempt was made to match characteristics of the finished filaments as in Part A. Final stretching of both materials described herein was adjusted so that they underwent identical amounts of stretch from the extrusion stage. This was done to investigate the effects of densification on equivalently stretched pieces of material from the same extrusion batch.

PTFE dispersion powder ("Fluon CD-123" resin produced by ICI America) was blended with 130 cc of "Isopar M" odorless solvent (produced by Exxon Corporation) per pound (287 cc/kg) of PTFE, compressed into a pellet, and extruded into a .108 inch (.274 cm) diameter rod in a ram extruder having a 153:1 reduction ratio in cross-sectional area from the pellet to the extruded filament.

The Isopar M was evaporated from a sample of the extruded filament. The density of this sample was 1.48 gm/cc and its matrix tensile strength was about 1,700 pounds per square inch (11.7 MPa).

The extruded filament still containing Isopar M was immersed in a container of Isopar M at 60°C and stretched seven-fold (600%) between capstans with an output velocity of about 57.6 ft/min (17.6 m/min). These capstans had a diameter of about 2.8 inches (7.1 cms) and a center-to-center distance of about 4.5 inches (11.4 cms). The diameter of the filament was reduced from about 0.108 inch (0.274 cm) to about .049 inch (.125 cm) by this stretching. The Isopar M was removed from this stretched material. The density of the stretched filament was 1.02 g/cc and the matrix tensile strength was about 7,900 pounds per square inch (54.5 MPa).

At this point the stretched filament was divided into two separate lots for further processing. Lot 661 was pulled through a densification die, while Lot 665 was not.

The stretched filament (Lot 661), from which the Isopar M had been removed, was then pulled through a circular

densification die heated to 300°C. The output velocity of the material exiting the die was about 1.9 ft/minute (.58 m/min). The opening in the die tapered at a 10° included angle from about .075 inch (.19 cm) diameter to .026 inch (.066 cm) diameter, and was then constant for a land length of about .026 inch (.066 cm).

The stretched filament (Lot 661), which had been pulled through the die, was then heated to 300°C and further stretched 4.5 fold (350%) between capstans with an output velocity of about 13 ft/min (3.96 m/min). These capstans had a diameter of about 2.8 inches (7.1 cms) and a center-to-center distance of about 24 inches (61 cms).

The stretched filament (Lot 665), which had not been pulled through the die, was heated in a 300°C oven and further stretched eight-fold (700%) between the same capstan setup just described, using an output velocity of about 11.5 ft/min (3.5 m/min).

Finally, both rods (filaments) were restrained from shrinking and heated in a 362°C oven for 60 seconds.

As illustrated by the pictures in Figures 13A and 13B and information in Table 5, these two types of material had vastly different microstructures. Lot 661 had much longer fibril lengths, and nodes where the H/W ratio was substantially larger than in the undensified (Lot 665) material. This example clearly illustrates that filaments which are densified prior to final stretching have much longer fibril lengths than do undensified filaments, when both materials undergo equivalent amounts of stretch.

These examples, Part A and B, demonstrate that densifying a stretched filament through the use of a densification die can result in a high strength material with a unique microstructure upon further stretching. The important aspect of the invention is that the stretched filament was densified to greater than or equal to about 2.0 g/cc prior to additional stretching.

TABLE 4

Finished filament characteristics		
	A-16 (Die)	3-1-3 (No die)
Density (g/cc)	.4	.5
Matrix tensile (psi) (MPa)	49,000 (338)	49,000 (338)
Diameter (inches) (cms)	.022 (.056)	.022 (.056)
Node width (μm)	17	9
Node height (μm)	102	16
H/W ratio	6	1.8
Fibril length (microns)	120	32
Total stretch ratio	79:1	52:1
Tissue ingrowth	collagen throughout interstices at 30 days	minimum collagen infiltration at 30 days

TABLE 5

Finished filament characteristics		
	661 (Die)	665 (No die)
Density (g/cc)	.6	.5
Matrix tensile (psi) (MPa)	55,000 (379.5)	64,000 (441.6)

TABLE 5 (continued)

Finished filament characteristics		
	661 (Die)	665 (No die)
Diameter (inches) (cms)	.022 (.059)	.025 (.064)
Node width (μm)	11	6
Node height (μm)	79	3
H/W ratio	7.2	.5
Fibril length (μm)	74	16
Total stretch ratio	58:1	57:1

To obtain the above listed densities, material volumes were calculated from diameter and length measurements, and this volume was divided into the weight of the material. Density calculations are accurate to two decimal places. Matrix tensile values were calculated as described above and are accurate to one decimal place. Diameters were measured using a non-contacting laser micrometer. The values listed represent the average diameter of several feet of material and are accurate to four decimal places.

To obtain node widths, node heights, and fibril lengths, pictures with a 200:1 magnification were used. The pictures were taken on a scanning electron microscope and a Nikon Biophot (Brightfield Microscope). Biophot is a trade mark. Measurements were taken with millimeter calipers and then converted to μm . Measurements were chosen (4 to 5 measurements per pictures for a given material type) by randomly drawing two horizontal lines on each picture approximately 1 inch (2.54 cms) apart. Five consecutive measurements were then taken, starting at the left margin. After obtaining 20 measurements, mean values were calculated. Node width, node height, and fibril length values are accurate to one decimal place. Total stretch ratio was calculated by dividing the dried filament extrudate weight/meter by the finished filament weight/meter. Ratios calculated are accurate to one decimal place.

Although the process of the present invention involves increasing the density of the dry extrudate to at least 1.75 gm/cc., the claims appended hereto define a porous material in other terms and accordingly not every porous material made in accordance with the process necessarily falls within the scope of all the appended claims.

Claims

1. A porous material consisting essentially of PTFE colvmer, which material has a microstructure having nodes interconnected by fibrils characterized in that, as measured along at least one direction, it has an average matrix tensile strength greater than 40,000 psi (276 MPa) and an average node height/width ratio greater than 3, an average fibril length greater than 15 μm , and the material is in filament form.
2. A porous material according to claim 1 characterized in that said average node height/width ratio is greater than 5.
3. A porous material according to claim 1 or 2 characterized in that it has average fibril length greater than 50 μm .
4. A porous material according to claim 1 or 2 characterised in that said average matrix tensile strength is about 49,000 psi (338 MPa), said average length is about 120 μm and said average node height/width ratio is about 6.
5. A porous material according to claim 1 or 2 characterised in that said average matrix tensile strength is about 55,000 psi (380 MPa), said average fibril length is about 74 μm , and said average node height/width ratio is about 7.
6. A porous material consisting essentially of polytetrafluoroethylene polymer, having nodes interconnected by fibrils, characterized in that said material has a matrix tensile strength greater than or equal to 3,000 psi (20.7 MPa) and less than or equal to 25,000 psi (172.5 MPa) and which has a corresponding coarseness index greater than or equal to the value on a line connecting the points A, B, C, and D defined in the following table:

Matrix tensile strength			Coarseness Index	
	psi	Mpa	gm/cc/psi	gm/cc/Mpa
A	3,000	20.7	0.40	57.97
B	12,000	82.8	0.40	57.97
C	16,000	110.4	0.20	29.0
D	25,000	172.5	0.20	29.0

5

10

and also having a crushability of less than 10%.

15

20

25

30

35

40

45

50

55

7. A porous material according to claim 6 characterized in that point C and point D have a coarseness index of 0.23 (gm/cc)/psi (33-35 gm/cc/MPa).
8. A porous material according to claim 6 characterised in that point C and point D have a coarseness index of 0.40 (gm/cc)/psi (57.97 gm/cc/MPa).
9. A porous material according to claim 6 characterized in that points A,B,C, and D have a coarseness index of 0.45 (gm/cc)/psi (65.25 gm/cc/MPa).
10. A porous material according to any one of claims 6 to 9 characterized in that it is film form.
11. A porous material according to claim 10 characterised in that it has a crushability less than 8%.
12. A porous material according to claim 10 characterised in that it has a crushability less than 5%.
13. A porous material consisting essentially of polytetrafluoroethylene polymer, having nodes interconnected by fibrils characterized in that it has an ethanol bubble point of less than or equal to 4.0 psi (27.5 kPa), said fibrils including first fibrils oriented substantially perpendicular to second fibrils, and the ratio of the matrix tensile strength as measured along the first fibril direction to the matrix tensile strength measured along the second fibril direction is between 0.4 and 2.5 and the matrix tensile strength in the weaker direction is greater than or equal to 3000 psi (20.7 MPa).
14. A porous material according to claim 13 characterized in that the ethanol bubble point is less than 3.0.
15. A porous material according to claim 13 characterized in that the ethanol bubble point is about 1.2.
16. A porous material according to any of claims 13 to 15 characterized in that the matrix tensile strength ratio is between 0.5 and 2.0.
17. A porous material according to claim 16 characterized in that the matrix tensile strength ratio is between 0.67 and 1.5.
18. A porous material according to any of claims 6 to 17 characterized in that it is in film form and that a significant number of the nodes extend across the film thickness.
19. A process for producing a porous material of polytetrafluoroethylene polymer, which material is in accordance with any one of the preceding claims, the material having been produced from paste-extruded polytetrafluoroethylene extrudate from which all extrusion-aid lubricant has been removed, characterized in that the process comprises the steps:

(a) increasing the density of the dry extrudate to at least 2.02 gm/cc at an elevated temperature less than the crystalline melt temperature of PTFE; and

(b) stretching said densified dry extrudate at an elevated temperature less than the crystalline melt temperature.

20. A process according to claim 19 characterized in that said densification step increases the dry extruded density to greater than 2.2 gm/cc.
- 5 21. A process according to claim 19 characterized in that said densification step increases the dry extrudate density to about its maximum value.
22. A process according to claim 19 characterized in that the densification step is accomplished by densifying the dry extrudate in a press.
- 10 23. A process according to claim 19 characterized in that the densification step is accomplished by calendering the dry extrudate.
24. A process according to claim 19 characterized in that the densification step is accomplished by drawing the dry extrudate through a densification die.
- 15 25. A process according to claim 19 characterized in that the densified dry extrudate is stretched uniaxially.
26. A process according to claim 19 characterized in that the densified dry extrudate is stretched biaxially.
- 20 27. A process according to claim 19 characterized in that the stretching step is carried out at about 300°C.
28. A process according to the claim 19 characterized in that the densification step is carried out at about 300°C.
- 25 29. A process according to claim 19 characterized in that it includes the step of heating the stretched article above the crystalline melt temperature while restraining the stretched article from shrinking.
- 30 30. A process according to any of claims 19, 23 or 24 characterized in that the densification and stretching steps are carried out continuously.
31. A process according to any one of claims 19 to 21 characterized by the step of stretching said dry extrudate before said densification step.

Patentansprüche

- 35 1. Poröses Material, das im wesentlichen aus PTFE-Polymer besteht, welches Material eine Mikrostruktur besitzt, die untereinander durch Fibrillen verbundene Knoten aufweist, dadurch gekennzeichnet, daß es, gemessen längs mindestens einer Richtung, eine mittlere Matrixzugfestigkeit von größer als 40 000 psi (276 MPa) und ein mittleres Verhältnis von Knotenhöhe/Breite von größer als 3 aufweist, eine mittlere Fibrillenlänge von größer als 15 µm besitzt und daß das Material in Fadenform vorliegt.
- 40 2. Poröses Material nach Anspruch 1, dadurch gekennzeichnet, daß das mittlere Verhältnis von Knotenhöhe/Breite größer als 5 ist.
- 45 3. Poröses Material nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß es eine mittlere Fibrillenlänge von größer als 50 µm aufweist.
4. Poröses Material nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die mittlere Matrixzugfestigkeit etwa 49 000 psi (338 MPa), die mittlere Länge etwa 120 µm und das mittlere Verhältnis Knotenhöhe/Breite etwa 6 betragen.
- 50 5. Poröses Material nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die mittlere Matrixzugfestigkeit etwa 55 000 psi (380 MPa), die mittlere Fibrillenlänge etwa 74 µm und das mittlere Verhältnis Knotenhöhe/Breite etwa 7 betragen.
- 55 6. Poröses Material, das im wesentlichen aus Polytetrafluorethylen-Polymer besteht, das untereinander durch Fibrillen verbundene Knoten aufweist, dadurch gekennzeichnet, daß das Material eine Matrixzugfestigkeit von größer als oder gleich 3 000 psi (20,7 MPa) und weniger als oder gleich 25 000 psi (172,5 MPa) aufweist und einen entsprechenden Grobheitsindex von größer als oder gleich dem Wert auf einer die in der folgenden Tabelle defi-

nierten Punkte A, B, C und D verbindenden Linie besitzt:

Matrixzugfestigkeit			Grobheitsindex	
	psi	MPa	g/cm ³ /psi	g/cm ³ /MPa
A	3 000	20,7	0,40	57,97
B	12 000	82,8	0,40	57,97
C	16 000	110,4	0,20	29,0
D	25 000	172,5	0,20	29,0

und ebenso eine Quetschbarkeit von weniger als 10% aufweist.

7. Poröses Material nach Anspruch 6, dadurch gekennzeichnet, daß Punkt C und Punkt D einen Grobheitsindex von 0.23 (g/cm³)/psi (33,35 g/cm³/MPa) aufweisen.
8. Poröses Material nach Anspruch 6, dadurch gekennzeichnet, daß Punkt C und Punkt D einen Grobheitsindex von 0.40 (g/cm³)/psi (57.97 g/cm³/MPa) aufweisen.
9. Poröses Material nach Anspruch 6, dadurch gekennzeichnet, daß die Punkte A, B, C und D einen Grobheitsindex von 0.45 (g/cm³)/psi (65,25 g/cm³/MPa) aufweisen.
10. Poröses Material nach einem der Ansprüche 6 bis 9, dadurch gekennzeichnet, daß es in Filmform vorliegt.
11. Poröses Material nach Anspruch 10, dadurch gekennzeichnet, daß es eine Quetschbarkeit von weniger als 8% aufweist.
12. Poröses Material nach Anspruch 10, dadurch gekennzeichnet, daß es eine Quetschbarkeit von weniger als 5% aufweist.
13. Poröses Material, daß im wesentlichen aus Polytetrafluorethylen-Polymer besteht, welches untereinander durch Fibrillen verbundene Knoten aufweist, dadurch gekennzeichnet, daß es einen Ethanolblasenpunkt von weniger als oder gleich 4,0 psi (27,6 kPa) aufweist, die Fibrillen erste Fibrillen einschließen, die im wesentlichen senkrecht zu zweiten Fibrillen orientiert sind, und das Verhältnis der Matrixzugfestigkeit, gemessen längs der ersten Fibrillenrichtung, zur Matrixzugfestigkeit, gemessen längs der zweiten Fibrillenrichtung, zwischen 0,4 und 2,5 beträgt, und die Matrixzugfestigkeit in der schwächeren Richtung größer als oder gleich 3 000 psi (20,7 MPa) ist.
14. Poröses Material nach Anspruch 13, dadurch gekennzeichnet, daß der Ethanolblasenpunkt weniger als 3,0 beträgt.
15. Poröses Material nach Anspruch 13, dadurch gekennzeichnet, daß der Ethanolblasenpunkt etwa 1.2 beträgt.
16. Poröses Material nach einem der Ansprüche 13 bis 15, dadurch gekennzeichnet, daß das Matrixzugfestigkeitsverhältnis 0,5 bis 2.0 beträgt.
17. Poröses Material nach Anspruch 16, dadurch gekennzeichnet, daß das Matrixzugfestigkeitsverhältnis 0,67 bis 1.5 beträgt.
18. Poröses Material nach einem der Ansprüche 6 bis 17, dadurch gekennzeichnet, daß es in Filmform vorliegt und sich eine signifikante Zahl der Knoten über die Filmdicke erstreckt.
19. Verfahren zum Herstellen eines porösen Materials aus Polytetrafluorethylen-Polymer, welches Material einem der vorhergehenden Ansprüche entspricht und welches Material aus pastenextrudiertem Polytetrafluorethylenextrudat gebildet wurde, aus dem sämtliches Extrusionshilfsgleitmittel entfernt worden ist, dadurch gekennzeichnet, daß das Verfahren die Schritte des
 - (a) Erhöhen der Dichte des trockenen Extrudats auf mindestens 2,02 g/cm³ bei einer erhöhten Temperatur, die niedriger als die Kristallschmelztemperatur des PTFE ist, und

(b) Streckens des verdichteten trockenen Extrudats bei erhöhter Temperatur, die niedriger als die Kristallschmelztemperatur ist,

umfaßt.

5

20. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Verdichtungsschritt die Dichte des trockenen Extrudats auf mehr als $2,2 \text{ g/cm}^3$ erhöht.

10

21. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Verdichtungsschritt die Dichte des trockenen Extrudats auf etwa ihren Maximalwert erhöht.

22. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Verdichtungsschritt durch Verdichten des trockenen Extrudats in einer Presse bewirkt wird.

15

23. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Verdichtungsschritt durch Kalandern des trockenen Extrudats bewirkt wird.

24. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Verdichtungsschritt durch Zehen des trockenen Extrudats durch eine Verdichtungsform bewirkt wird.

20

25. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß das verdichtete trockene Extrudat uniaxial gestreckt wird.

25

26. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß das verdichtete trockene Extrudat biaxial gestreckt wird.

27. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Streckschritt bei etwa 300°C durchgeführt wird.

30

28. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Verdichtungsschritt bei etwa 300°C durchgeführt wird.

35

29. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß es den Schritt des Erhitzens des gestreckten Gegenstandes auf oberhalb der Kristallschmelztemperatur einschließt, während der gestreckte Gegenstand am Schrumpfen gehindert wird.

30. Verfahren nach einem der Ansprüche 19, 23 oder 24, dadurch gekennzeichnet, daß der Verdichtungs- und Streckschritt kontinuierlich durchgeführt werden.

40

31. Verfahren nach einem der Ansprüche 19 bis 21, gekennzeichnet durch den Schritt des Streckens des trockenen Extrudats vor dem Verdichtungsschritt.

Revendications

45

1. Matériau poreux se composant essentiellement de polymère de polytétrafluoréthylène (PTFE), lequel matériau a une microstructure ayant des noeuds interconnectés par des fibrilles caractérisé en ce que, comme mesuré le long d'au moins une direction, il présente une résistance à la traction matricielle moyenne supérieure à 40 000 psi (276 Mpa) et un rapport hauteur/largeur de noeud moyen supérieur à 3, une longueur de fibrille moyenne supérieure à $15 \mu\text{m}$, et le matériau est sous forme de filament.

50

2. Matériau poreux selon la revendication 1, caractérisé en ce que ledit rapport hauteur/largeur de noeud moyen est supérieur à 5.

55

3. Matériau poreux selon la revendication 1 ou 2, caractérisé en ce qu'il présente une longueur de fibrille moyenne supérieure à $50 \mu\text{m}$.

4. Matériau poreux selon la revendication 1 ou 2, caractérisé en ce que ladite résistance à la traction matricielle moyenne est d'environ 49 000 psi (338 Mpa), ladite longueur moyenne est d'environ $120 \mu\text{m}$ et ledit rapport hauteur/

largeur de noeud moyen est d'environ 6.

5. Matériau poreux selon la revendication 1 ou 2, caractérisé en ce que ladite résistance à la traction matricielle moyenne est d'environ 55 000 psi (380 MPa), ladite longueur de fibrille moyenne est d'environ 74 μm , et ledit rapport hauteur/largeur de noeud moyen est d'environ 7.

6. Matériau poreux se composant essentiellement de polymère de polytétrafluoréthylène, ayant des noeuds interconnectés par des fibrilles, caractérisé en ce que ledit matériau a une résistance à la traction matricielle supérieure ou égale à 3000 psi (20,7 MPa) et inférieure ou égale à 25 000 psi (172,5 MPa) et qui a un indice de grosseur correspondant supérieur ou égal à la valeur sur une ligne reliant les points A, B, C et D définis dans le tableau suivant :

	Résistance à la traction matricielle		Indice de grosseur	
	psi	MPa	g/cm ³ /psi	g/cm ³ /MPa
A	3000	20,7	0,40	57,97
B	12 000	82,8	0,40	57,97
C	16 000	110,4	0,20	29,0
D	25 000	172,5	0,20	29,0

et ayant également une aptitude au concassage inférieure à 10 %.

7. Matériau poreux selon la revendication 6, caractérisé en ce que le point C et le point D ont un indice de grosseur de 0,23 (g/cm³/psi) (33 à 35 g/cm³/MPa).

8. Matériau poreux selon la revendication 6, caractérisé en ce que le point C et le point D ont un indice de grosseur de 0,23 (g/cm³/psi) (57,97 g/cm³/MPa).

9. Matériau poreux selon la revendication 6, caractérisé en ce que les points A, B, C et D ont un indice de grosseur de 0,45 (g/cm³/psi) (65,25 g/cm³/MPa).

10. Matériau poreux selon l'une quelconque des revendications 6 à 9, caractérisé en ce qu'il est sous forme de film.

11. Matériau poreux selon la revendication 10, caractérisé en ce qu'il a une aptitude au concassage inférieure à 8 %.

12. Matériau poreux selon la revendication 10, caractérisé en ce qu'il a une aptitude au concassage inférieure à 5 %.

13. Matériau poreux se composant essentiellement de polymère de polytétrafluoréthylène, ayant des noeuds interconnectés par des fibrilles, caractérisé en ce qu'il a un point de bulle de l'éthanol inférieur ou égal à 4,0 psi (27,5 kPa), lesdites fibrilles comprenant lesdites fibrilles orientées sensiblement perpendiculairement aux secondes fibrilles, et le rapport de la résistance à la traction matricielle telle que mesurée le long de la première direction des fibrilles jusqu'à la résistance à la traction matricielle mesurée le long de la seconde direction des fibrilles, est compris entre 0,4 et 2,5 et la résistance à la traction dans la direction la plus faible est supérieure ou égale à 3000 si (20,7 MPa).

14. Matériau poreux selon la revendication 13, caractérisé en ce que le point de bulle de l'éthanol est inférieur à 3,0.

15. Matériau poreux selon la revendication 13, caractérisé en ce que le point de bulle de l'éthanol est d'environ 1,2.

16. Matériau poreux selon l'une quelconque des revendications 13 à 15, caractérisé en ce que le rapport de résistance à la traction matricielle est compris entre 0,5 et 2,0.

17. Matériau poreux selon la revendication 16, caractérisé en ce que le rapport de résistance à la traction matricielle est compris entre 0,67 et 1,5.

18. Matériau poreux selon l'une quelconque des revendications 6 à 17, caractérisé en ce qu'il est sous forme de film et en ce qu'un nombre important de noeuds s'étend sur l'épaisseur du film.

19. Procédé pour fabriquer un matériau poreux en polymère de polytétrafluoréthylène, lequel matériau est, conformément à l'une quelconque des revendications précédentes, le matériau qui est fabriqué à partir d'extrudat de polytétrafluoréthylène extrudé sous forme de pâte à partir duquel tout lubrifiant aidant à l'extrusion a été éliminé, caractérisé en ce que le procédé comprend les étapes consistant à :

5

(a) augmenter la densité de l'extrudat sec jusqu'à au moins $2,02 \text{ g/cm}^3$ à une température élevée inférieure à la température de fusion cristalline du PTFE ; et

(b) étirer ledit extrudat sec densifié à une température élevée inférieure à la température de fusion cristalline.

10

20. Procédé selon la revendication 19, caractérisé en ce que ladite étape de densification augmente la densité de l'extrudat sec à plus de $2,2 \text{ g/cm}^3$.

21. Procédé selon la revendication 19, caractérisé en ce que l'étape de densification augmente la densité de l'extrudat sec d'environ sa valeur maximale.

15

22. Procédé selon la revendication 19, caractérisé en ce que l'étape de densification est réalisée en densifiant l'extrudat sec dans une presse.

20

23. Procédé selon la revendication 19, caractérisé en ce que l'étape de densification est réalisée en calandrant l'extrudat sec.

24. Procédé selon la revendication 19, caractérisé en ce que l'étape de densification est réalisée en étirant l'extrudat sec à travers une matrice de densification.

25

25. Procédé selon la revendication 19, caractérisé en ce que l'extrudat sec densifié est allongé de manière uniaxiale.

26. Procédé selon la revendication 19, caractérisé en ce que l'extrudat sec densifié est allongé de manière biaxiale.

30

27. Procédé selon la revendication 19, caractérisé en ce que l'étape d'allongement est réalisée à environ 300°C .

28. Procédé selon la revendication 19, caractérisé en ce que l'étape de densification est réalisée à environ 300°C .

35

29. Procédé selon la revendication 19, caractérisé en ce qu'il comprend l'étape consistant à chauffer l'article allongé au-delà de la température de fusion cristalline tout en modérant la contraction de l'article allongé.

30. Procédé selon l'une quelconque des revendications 19, 23 ou 24, caractérisé en ce que les étapes de densification et d'allongement sont réalisées en continu.

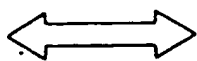
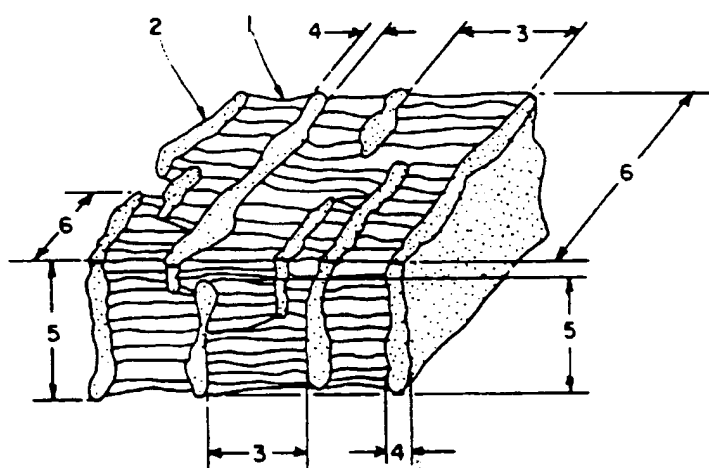
40

31. Procédé selon l'une quelconque des revendications 19 à 21, caractérisé par l'étape consistant à allonger ledit extrudat sec avant ladite étape de densification.

45

50

55



DIRECTION OF UNIAXIAL STRETCHING

FIG. 1

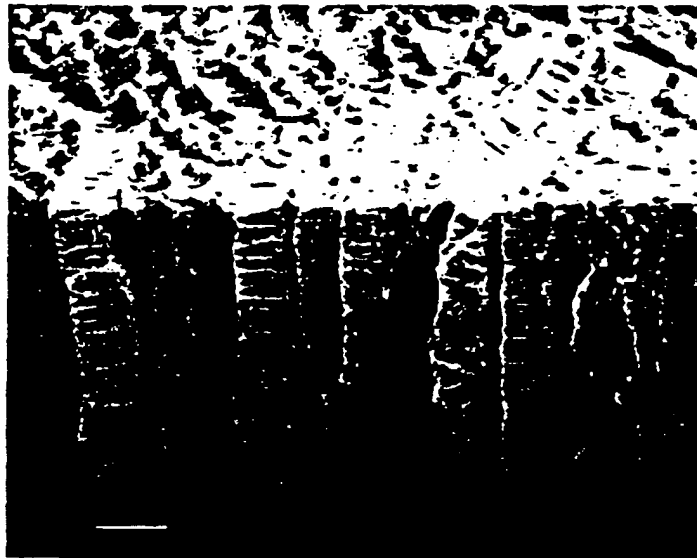


FIG. 2

BEST AVAILABLE COPY

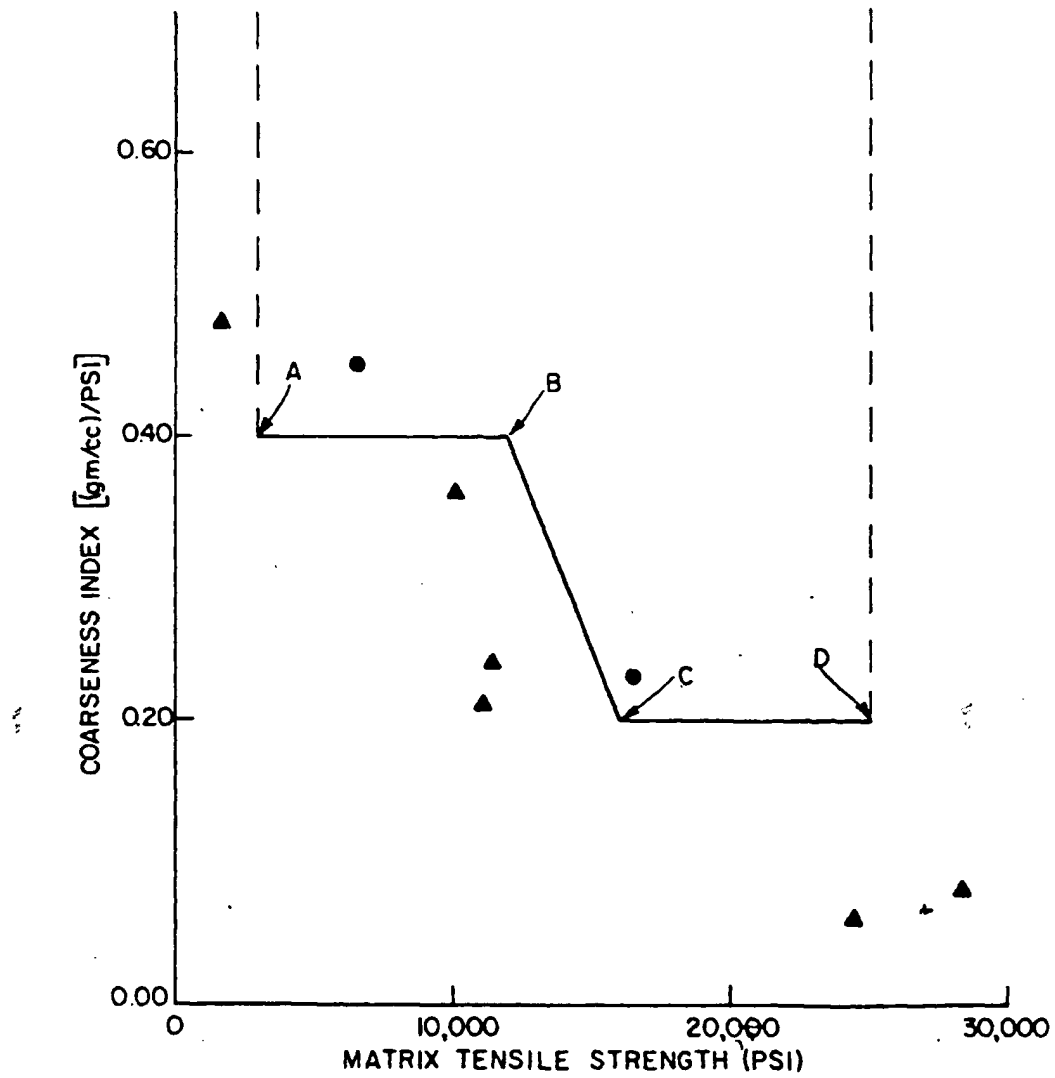


FIG. 3

LEGEND
 ● PRESENT INVENTION
 ▲ PRIOR ART

BEST AVAILABLE COPY

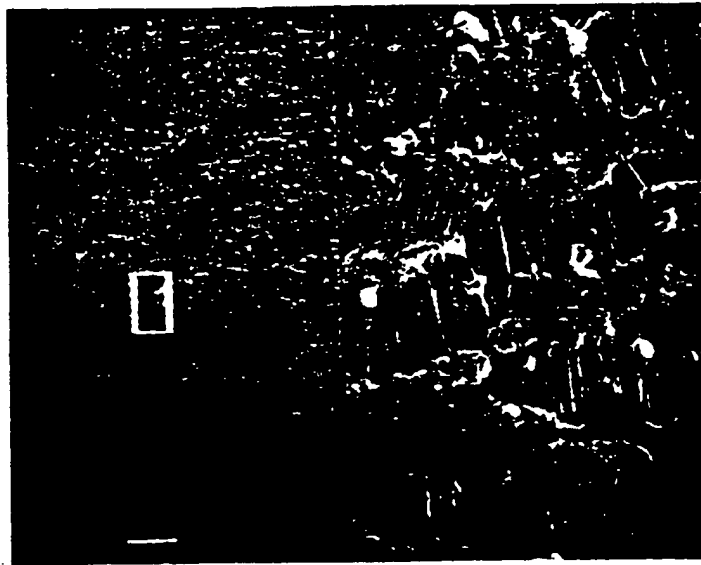


FIG. 4

BEST AVAILABLE COPY

25 c



FIG. 5

BEST AVAILABLE COPY

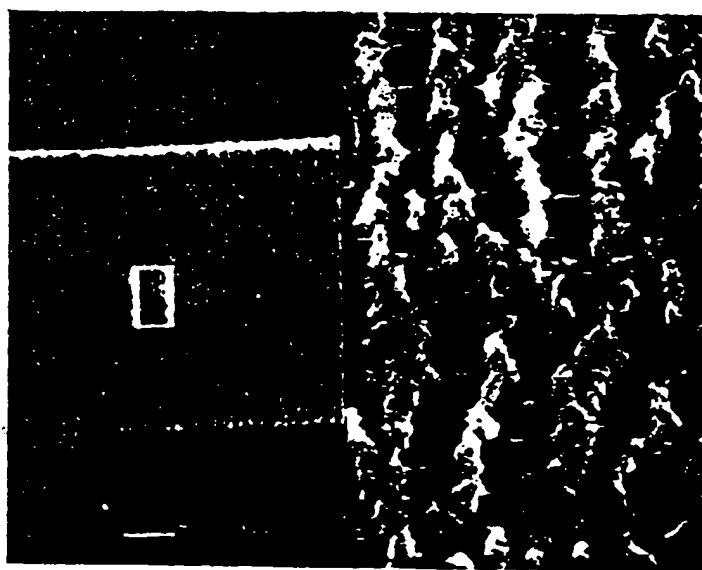


FIG. 6

BEST AVAILABLE COPY



FIG. 7

BEST AVAILABLE COPY

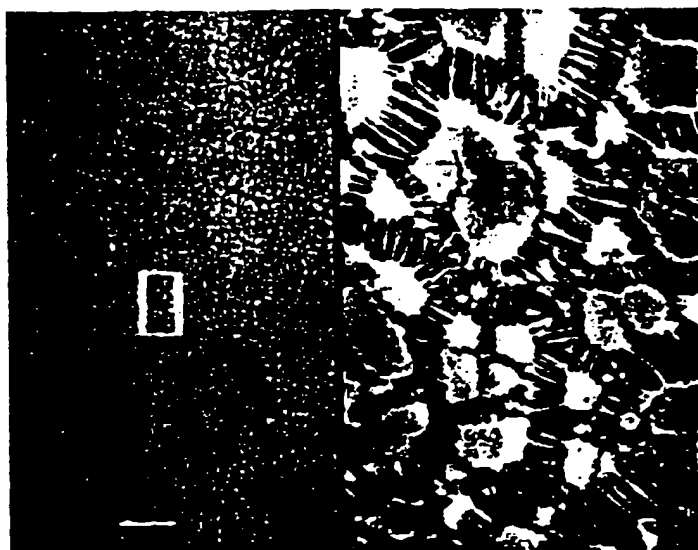


FIG. 8

BEST AVAILABLE COPY

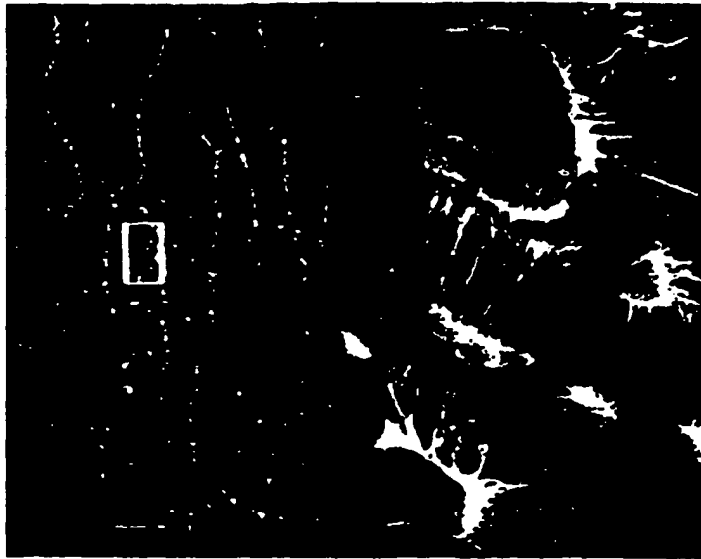


FIG. 9

BEST AVAILABLE COPY

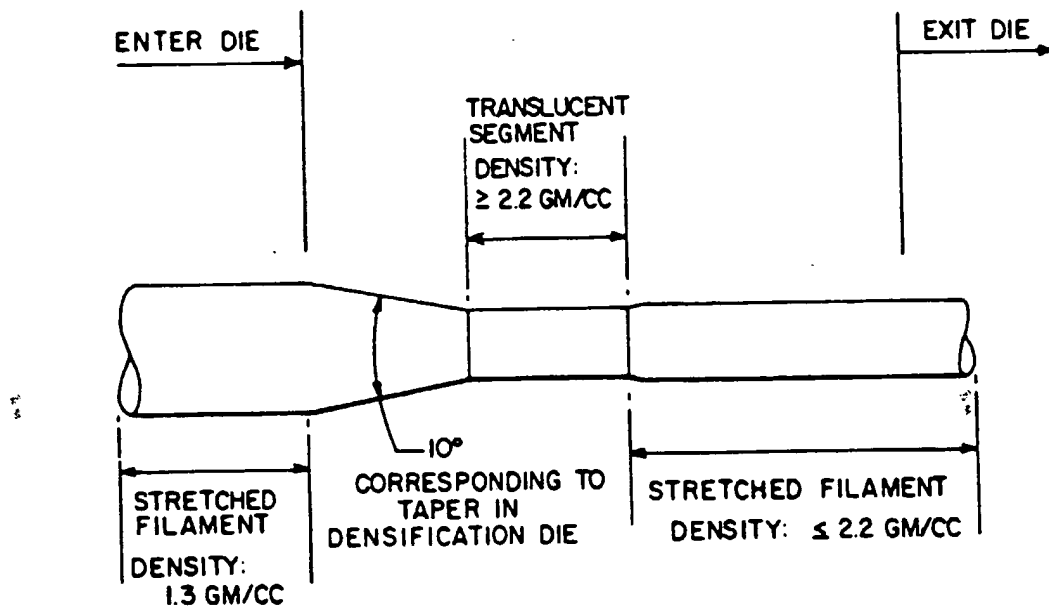
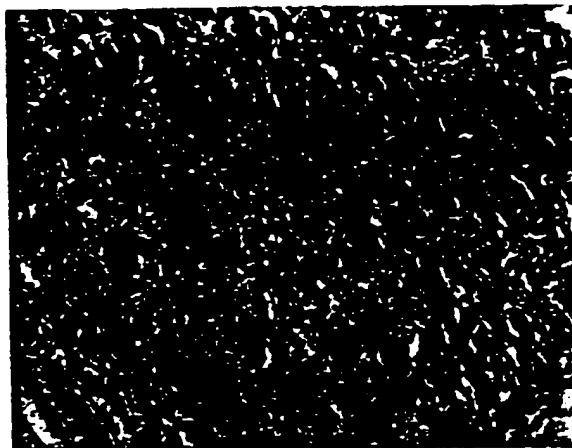


FIG. 10

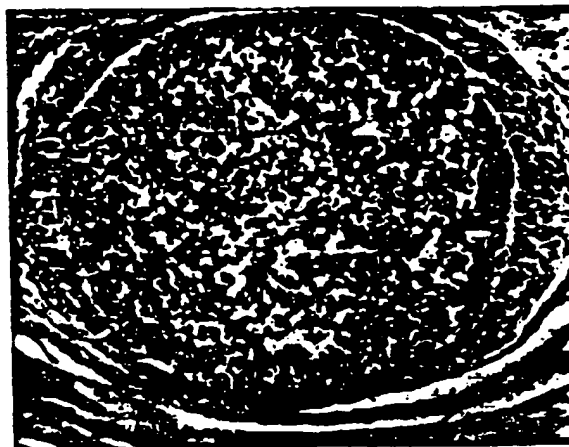
BEST AVAILABLE COPY

Figure 11A



B-26

Figure 11B



B-13

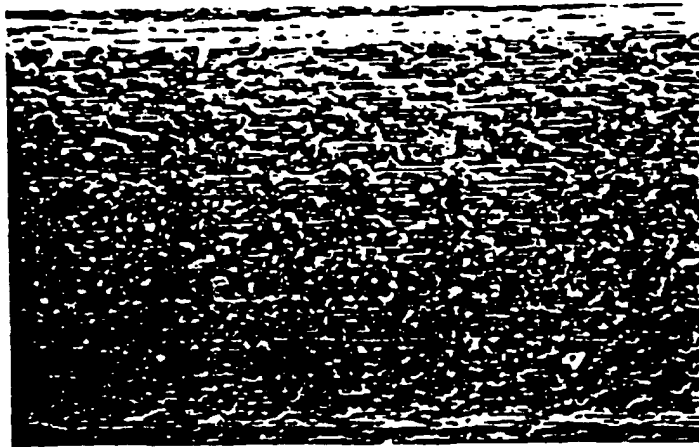
BEST AVAILABLE COPY

Figure 12A



A-16

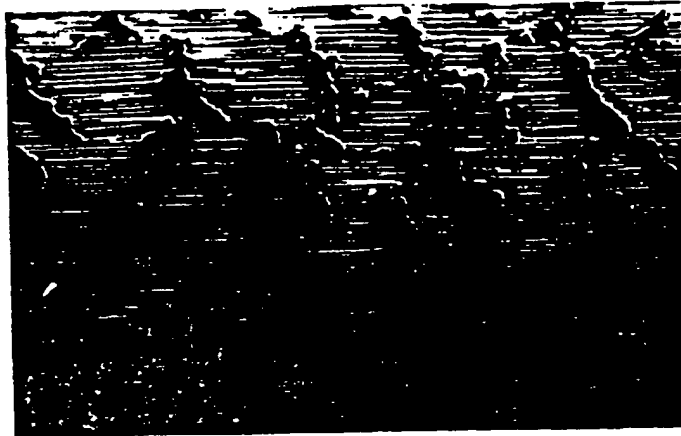
Figure 12B



B-1-3

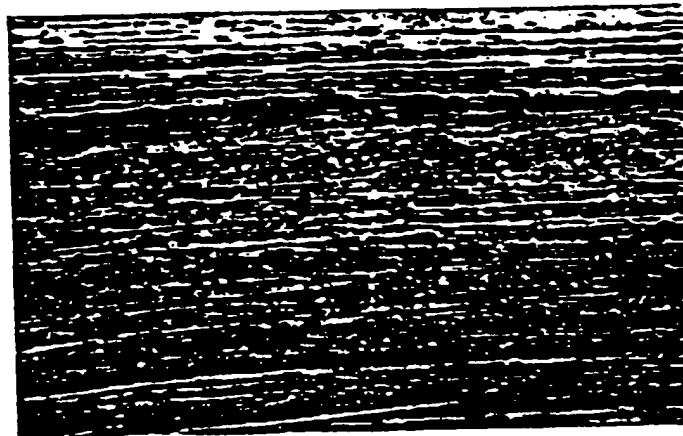
BEST AVAILABLE COPY

Figure 13A



Lot 661

Figure 13B



Lot 665

BEST AVAILABLE COPY